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(54) **Polyvalent metal salts of salicyclic acid resin and process for the preparation thereof**

(57) The present invention relates to a process for preparing polyvalent metal salts of salicyclic acid resin, comprising reacting salicyclic acid or its derivative and styrene or its derivative in the presence of zinc salt of organic carboxylic acid and/or polyvalent metal compound at 50 to 200 °C to prepare the reaction product, and reacting the reaction product with polyvalent metal compound; an aqueous dispersion where the polyvalent metal salt of resin is dispersed in water; and to a color development sheet prepared from the polyvalent metal salts of salicyclic acid resin.

EP 1 072 623 A2

Description

Field of the Invention

5 [0001] The present invention relates to a polyvalent metal salt of salicylic acid resin, which is used as a color developer for recording material such as pressure-sensitive copying paper, and to a process for the preparation thereof. Furthermore, it relates to an aqueous dispersion and a color development sheet prepared from the polyvalent metal salts of salicylic acid resin.

10 Background of the Invention

[0002] It is known that metal salts of salicylic acid derivative are useful as color developers for pressure-sensitive copying paper, and numbers of preparation processes and uses thereof were proposed. For example,

- 15 1) 3,5-disubstituted salicylic acid derivative is prepared from the reaction of 2,4-disubstituted-phenol derivative with carbon dioxide by Kolbe-Schmitt reaction (Japanese Patent Publication No. 76-25174 and U.S. Patent No. 3,983,292). In this method, however, two-step process is needed to prepare 3,5-disubstituted salicylic acid derivative from phenol, and high-temperature high-pressure facility is required in the reaction with carbon dioxide. In addition, in case of using as color developer the metal salts of 3,5-disubstituted salicylic acid derivative such as zinc salt of 3,5-di(α -methylbenzyl)salicylic acid, developed image might be lost on water contact.
- 20 2) 4-[α -methylbenzyl(α -methylbenzyl)]salicylic acid derivative is prepared by reacting 1 mole of salicylic acid with 2 moles or more of phenylethanol derivatives (Japanese Patent Publication No. 93-61110 and U.S. Patent No. 4,754,063).
- 25 3) Polyvalent metal salts of 3,5-di(α -ethylbenzyl)salicylic acid derivative and polyvalent metal salts of 4-[α -methylbenzyl(α -methylbenzyl)]salicylic acid derivative are prepared by reacting 1 mole of salicylic acid with 2 moles or more of styrene derivatives in the presence of aromatic sulfonic acid, and reacting the reaction product thus prepared with polyvalent metal salts of inorganic acid or lower aliphatic carboxylic acid (Japanese Patent Publication 93-75736 and U.S. Patent No. 4,748,259). However, in case of using the polyvalent metal salts (e.g., zinc salts) of 4-[α -methylbenzyl(α -methylbenzyl)]salicylic acid thus prepared as color developer for pressure-sensitive copying paper, developed image might be lost on water contact.
- 30 4) 3,5-di(α -methylbenzyl)salicylic acid derivative is prepared by a reaction of salicylic acid with styrene in the presence of aliphatic carboxylic acid using organic sulfonic acid or inorganic acid as a catalyst (Japanese Patent Application Laid-open Publication No. 90-91043). However, in case of using the polyvalent metal salts of 3,5-di(α -methylbenzyl)salicylic acid (e.g., zinc salt) as color developer, developed image might be lost on water contact.
- 35 5) A process for preparing metal salts of polymeric salicylic acid resin by reacting salicylic acid derivative with styrene derivative in the presence of acid catalyst at 40-170°C, and reacting the reaction product with metal salt of fatty acid (Japanese Patent Application Laid-open No. 88-142537 and U.S. Patent No. 4,929,710). However, the metal salts of salicylic acid resin thus prepared have drawbacks in that it sometimes has coloring and its dispersion is liable to coagulate because of the difficulty in making fine particles at dispersion.
- 40 6) A process for preparing polyvalent metal salts of salicylic acid resin is disclosed, which comprises reacting salicylic acid ester with styrene, hydrolyzing the reaction product thus obtained, and then reacting with polyvalent metal compound (Japanese Patent Application Laid-open Publication No. 89-133780 and U.S. Patent No. 4,952,648). However, the thus prepared polyvalent metal salts (e.g., zinc salts) of salicylic acid resin are disadvantageous in that its dispersion tends to coagulate due to the difficulty in making fine particles at dispersion.
- 45 7) A process for producing polyvalent metal salts of salicylic acid resin is disclosed, which comprises reacting salicylic acid or its derivative with styrene or its derivative in the presence of sulfuric acid at -20 to 40°C, and further reacting with polyvalent metal compound (Japanese Patent Application Laid-open Publication No. 95-228042 and U.S. Patent No. 5525686). However, despite that the color developer thus obtained is improved of its physical properties, various problems still exist, such as complicated reaction process, environmental pollution, and productivity decrease due to low yield. Further, when preparing an aqueous dispersion using the metal salts, the average particle size of the metal salts is at most 1.5 μ m.
- 50

[0003] As described above, reaction products and their polyvalent metal salts thereof obtained from the reaction of salicylic acid derivative with styrene derivative show different physical properties depending on the reaction conditions (e.g., catalyst, solvent, reaction temperature). Therefore, it is impossible to determine the physical properties of the salicylic acid resin and polyvalent metal salts thereof by a theoretical method, or too difficult to infer them based on experiments. At present, it is expected to establish their physical properties through experiment procedures.

[0004] Lately, there has been a desire for a color developer advantageous in that it is easily brought into fine parti-

cles at dispersion, resulting dispersion has high storage stability, and developed image shows superior storage stability, high resistance to water and to abrasion when forming a color development sheet for pressure-sensitive copying paper using the color developer.

[0005] As a result of intensive studies to solve the problems in the prior art as described above, the present inventor discovered that polyvalent metal salts of salicylic acid resin having superior physical properties could be produced in high yield under a specific catalyst, not an acid catalyst, and specific temperature.

Summary of the Invention

[0006] An object of the present invention is to provide a process for preparing polyvalent metal salts of salicylic acid resin.

[0007] It is another object of the present invention to provide polyvalent metal salts of salicylic acid resin prepared by the process.

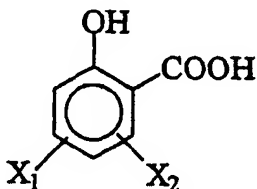
[0008] It is a further object of the present invention to provide an aqueous dispersion of polyvalent metal salts of salicylic acid resin prepared by the process.

[0009] It is a further object of the present invention to provide a color development sheet prepared by the process, where the developed image has superior storage stability, high resistance to water and to abrasion.

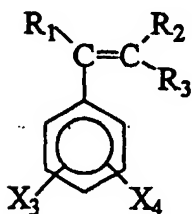
Detailed Description of the Invention

[0010] The present invention provides a process for preparing polyvalent metal salts of salicylic acid resin, comprising:

reacting salicylic acid of the formula 1 or its derivative and styrene of the formula 2 or its derivative in the presence of zinc salt of organic carboxylic acid or polyvalent metal compound or a mixture thereof at 50-200°C, reacting the resulting reaction product with polyvalent metal compound.



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wherein, X_1 and X_2 is hydrogen, alkyl, alkoxy or halogen, respectively, and each of R_1 , R_2 and R_3 is hydrogen or alkyl, and X_3 and X_4 is hydrogen, alkyl, alkoxy, aralkyl, aryl or halogen, respectively.

[0011] For the compound of formula 1, each of X_1 and X_2 is preferably hydrogen, C1-C12 alkyl, C1-C12 alkoxy, F, Cl or Br, and more preferably hydrogen.

[0012] Examples of the compound of formula 1, though not limited, include salicylic acid, 3-methylsalicylic acid, 4-methylsalicylic acid, 5-methylsalicylic acid, 3-n-butylsalicylic acid, 6-methylsalicylic acid, 6-ethylsalicylic acid, 5-isopropylsalicylic acid, 4-n-pentylsalicylic acid, 5-cyclohexylsalicylic acid, 5-n-octylsalicylic acid, 5-t-octylsalicylic acid, 4-non-

ylsalicylic acid, 5-nonylsalicylic acid, 4-n-dodecylsalicylic acid, 4-methoxysalicylic acid, 6-methoxysalicylic acid, 5-ethoxysalicylic acid, 4-n-hexyloxysalicylic acid, 5-fluorosalicylic acid, 3-chlorosalicylic acid, 4-chlorosalicylic acid, 5-chlorosalicylic acid and 5-bromosalicylic acid.

5 [0013] The above salicylic acid derivatives may be used individually or in combination of two or more. Among them, salicylic acid or alkyl substituted salicylic acid derivative such as 3-methylsalicylic acid is preferable, and salicylic acid is especially preferred.

[0014] For the compound of formula 2, each of X_3 and X_4 is preferably hydrogen, C1-C12 alkyl, C1-C12 alkoxy, C1-C10 aralkyl, C6-C10 aryl, F, Cl or Br, and most preferably X_3 and X_4 are both hydrogen. Also, each of R_1 , R_2 and R_3 is preferably hydrogen or C1-C4 alkyl, and most preferably hydrogen.

10 [0015] Examples of the compound of formula 2, though not limited to, include styrene, 2-methylstyrene, 3-methylstyrene, 4-methylstyrene, 2-ethylstyrene, 4-ethylstyrene, 3-isopropylstyrene, 4-isopropylstyrene, 4-n-butylstyrene, 4-*t*-butylstyrene, 4-cyclohexylstyrene, 4-n-octylstyrene, 4-n-decylstyrene, 2,4-dimethylstyrene, 2,5-dimethylstyrene, 3-methoxystyrene, 4-methoxystyrene, 4-ethoxystyrene, α -methylstyrene, α -ethylstyrene, α -n-butylstyrene, α -isobutylstyrene, α , β -dimethylstyrene, α , β -diethylstyrene, α -methyl- β -isopropylstyrene, α -n-propyl- β -methylstyrene, 4-(α , α -dimethylbenzyl)styrene, 4-phenylstyrene, 4-fluorostyrene, 2-chlorostyrene, 3-chlorostyrene, 4-chlorostyrene and 4-bromostyrene.

15 [0016] The above styrene derivatives may be used individually or in combination of two or more. Among them, styrene or alkyl substituted styrene derivatives such as 4-methylstyrene, or α -methylstyrene is preferable, and styrene is the most preferably used.

20 [0017] Hereinafter, each step of the process for the present invention will be described in detail.

Reaction A: Step of reacting a compound of formula 1 with a compound of formula 2

[0018] The compound of formula 2 is reacted in an amount of 1 to 9 moles, preferably 1.5 to 7 moles, and most preferably 1.6 to 6 moles to 1 mole of the compound of formula 1.

[0019] The reaction A is conducted in the presence of zinc salt of organic carboxylic acid and/or polyvalent metal compound. The kind and the amount of used zinc salt of organic carboxylic acid and polyvalent metal compound is not particularly limited, but a large amount of use may cause an adverse effect on the properties of the reaction products or decrease working efficiency and production efficiency.

30 [0020] Therefore, adequate amount of zinc salt of organic carboxylic acid and polyvalent metal compound may be at least 0.05% by weight, preferably 0.5-50% by weight based on the weight of the compound of formula 1. Further, higher purity in the zinc salt of organic carboxylic acid and polyvalent metal compound is preferred. As zinc salt of organic carboxylic acid, zinc benzoate, zinc caprylate, zinc stearate and zinc acetate may be used, and as polyvalent metal compound, water-soluble or insoluble metal compound having valence of 2, 3 and 4 may be used. Examples of polyvalent metal compound include sulfates such as zinc sulfate, magnesium sulfate, calcium sulfate and aluminum sulfate, chlorides such as zinc chloride, magnesium chloride, calcium chloride, barium chloride, nickel chloride, cobalt chloride and aluminum chloride, acetates such as zinc acetate and manganese acetate, nitrate such as zinc nitrate, oxides such as zinc oxide, and hydroxides such as zinc hydroxide.

40 [0021] In the step of the Reaction A, there is no particular limit on the reaction operation. The zinc salt of organic carboxylic acid or polyvalent metal compound or a mixture thereof, and a compound of formula 1 may be mixed in a reaction vessel, and then a compound of formula 2 is added to the mixture. Otherwise, the organic carboxylic acid zinc salt and/or polyvalent metal compound, a compound of formula 1, and a part of compound of formula 2 are mixed in a reaction vessel, and then the rest of the compound of formula 2 is added to the mixture. Further, the substances mentioned above may be added at one time.

45 [0022] The rest of compound of formula 2 may be added continuously or intermittently using known means (e.g., dropper and measuring pump). Of course, other methods may be applied, as far as it is applicable in terms of process technology.

[0023] The adding period of the compound of formula 2 is not particularly limited, but is generally about 0.5 to 13 hours, preferably about 1 to 9 hours.

50 [0024] It is preferable to conduct reaction A with stirring in order to increase the reaction efficiency. The stirring apparatus is not particularly limited, but it is preferable to use one having sufficient stirring power to guarantee the reaction efficiency. As an example of such apparatus, there is a tank-typed reaction apparatus and tubular reaction apparatus with stirrer such as propeller stirrer, turbine stirrer, paddle stirrer, homogenizer, homomixer, line mixer or linehorn mixer. The reaction A may be conducted in a batch process or continuously.

55 [0025] The reaction temperature of the reaction A may be 50-200°C, and preferably 120-180°C.

[0026] In case of dropping compound of formula 2, reaction period is longer than adding period, and after adding the compound, the solution may be left or subjected to stirring at 50-200°C for the time. Usually, the reaction may be carried out for 0.5 to 20 hours, preferably for 1 to 12 hours.

[0027] Generally, reaction A may be carried out in atmosphere, and if necessary, reduced or elevated pressure may be adopted. For example, the reaction may be conducted in the air, or in the presence of inert gas (e.g., nitrogen, helium or argon gas).

[0028] Resin prepared by reaction A (hereinafter, "Resin A") may be used in subsequent reaction (Reaction B) with polyvalent metal compound.

[0029] Resin A is a resin having complicated compounds consisting of various compounds formed by various reactions of reactive oligomers.

Reaction B: Step of reacting the reaction product from Reaction A with polyvalent metal compound

[0030] Polyvalent metal salts of salicylic acid resin of the present invention may be prepared by a reaction of Resin A and polyvalent metal compound. There is no particular limit on the reaction process. For example, melting Resin A and polyvalent metal compound (e.g., oxides, hydroxides, carbonates, silicates or organic carboxylate of polyvalent metal) (Melting method), or reacting alkali metal salts, amine salts or ammonium salts of Resin A with polyvalent metal compound in water (Double decomposition method) may be used. Preferably, melting method is used to prepare polyvalent metal salts of salicylic acid resin of the present invention.

[0031] In case of conducting Reaction B by melting method, Resin A is heat-melted together with oxide, hydroxide, carbonate or silicate of polyvalent metal with polyvalent metal salts of organic carboxylic acid such as zinc chloride, zinc carboxylate, zinc stearate, zinc benzoate at 50-200°C for 1-10 hours. In this case, a basic substance such as ammonium acetate, ammonium carboxylate, ammonium stearate and ammonium benzoate may be added.

[0032] As polyvalent metal compound, water-soluble or insoluble metal compound having valence of 2, 3 or 4 may be used. Examples of the polyvalent metal compound include sulfates such as zinc sulfate, magnesium sulfate, calcium sulfate and aluminum sulfate, chlorides such as zinc chloride, magnesium chloride, calcium chloride, barium chloride, nickel chloride, cobalt chloride and aluminum chloride, acetates such as zinc acetate, manganese acetate and nitrates such as zinc nitrate, oxides such as zinc oxide, hydroxides such as zinc hydroxide, and these compounds may be used individually or in combination of two or more.

[0033] Polyvalent metal compound may be used in solid forms or in aqueous solution.

[0034] The amount of the polyvalent metal compound used is 0.6 to 1.6 equivalents, and preferably 0.8 to 1.2 equivalents to 1 equivalent of Resin A. Herein, when polyvalent metal compound is a metal compound of valence 2 (e.g., zinc oxide), 1 equivalent of polyvalent metal compound means 0.5 mole of metal compound of valence 2 to 1 mole of resin A.

[0035] Polyvalent metal salts of salicylic acid resin according to the present invention may also be prepared by reacting salicylic acid of formula 1 or its derivative with styrene of formula 2 or its derivative in the presence of polyvalent metal compound or a mixture of polyvalent metal compound and zinc salt of organic carboxylic acid at 50-200°C. Herein, the amount of all the substances is the same as described above.

[0036] The resulting polyvalent metal salts of salicylic acid resin of the present invention is a resin obtained from the reaction of Resin A and polyvalent metal compound, and its composition is far more complicated than Resin A.

[0037] Molecular weight of the polyvalent metal salts of salicylic acid resin in the present invention depends on the amount of the compounds of formulae 1 and 2, and reaction conditions, but when used as a color developer for pressure-sensitive copying paper, it is preferably 300-2000, and more preferably, 400-1300.

[0038] The polyvalent metal salts of salicylic acid resin of the present invention have softening point of 50 —130°C.

[0039] The present invention further provides an aqueous dispersion where polyvalent metal salts of salicylic acid resin thus prepared are dispersed in water.

[0040] Further, the present invention provides a color development sheet prepared from the above polyvalent metal salts of salicylic acid resin.

[0041] Hereinafter, the aqueous dispersion and the color development sheet for pressure-sensitive copying paper prepared from the polyvalent metal salts of salicylic acid resin as developer will be described.

[0042] Aqueous dispersion may be obtained by the following methods:

- 1) Method of obtaining the desired aqueous dispersion by grinding polyvalent metal salts of salicylic acid resin using dispersion apparatus such as ball mill, sand grinder, dynamill, high speed impeller dispersing apparatus or annular mill.
- 2) Method of obtaining the desired aqueous dispersion by dissolving polyvalent metal salts of salicylic acid resin in an organic solvent, emulsifying in an aqueous medium using ultrasonic dispersing machine, homogenizer, homomixer or line homomixer and by eliminating the organic solvent.
- 3) Method of obtaining the desired aqueous dispersion by directly adding emulsifying dispersant to polyvalent metal salts of salicylic acid resin and stirring with high speed.

[0043] The emulsifying dispersant that can be used in an aqueous medium includes ionic or nonionic surfactant. For example, synthetic or natural polymeric compounds such as polyvinyl alcohol, alkyl denaturated polyvinyl alcohol, cyanoethyl denaturated polyvinyl alcohol, ether denaturated polyvinyl alcohol, polyacrylamide, polyacrylic acid, acrylamide-alkylacrylate copolymer, alkali metal salt of polystyrenesulfonic acid, maleic acid anhydride-isobutylene copolymer, carboxymethylcellulose, hydroxyethylcellulose, polyvinylpyrrolidone, starch and its derivative, casein, Arabic rubber, agar and gelatin; alkali metal salts of alkylbenzenesulfonic acid; alkali metal salts of alkylnaphthalenesulfonic acid; alkali metal salts of dialkylsulfosuccinic acid; alkali metal salts of alkylsulfonic acid; polyoxyethylene alkyl ether; polyoxyethylene alkyl phenyl ether and polyhydroxy alcohol fatty acid ester. These emulsifying dispersants may be used individually or in combination of two or more. No special limit exists on the amount used, but it is generally 0.5-25 parts per weight to 100 parts of polyvalent metal salts of salicylic acid resin.

[0044] Though no special limit exists on the amount of water when preparing aqueous dispersion, concentration of the color developer in aqueous dispersion should be in the range of 10-60% by weight, preferably, 20-50% by weight.

[0045] When using the aqueous dispersion of the color developer thus obtained as coating liquid to form a color developer layer on support, binder and pigments may be added thereto.

[0046] There is no special limit on the kinds of binder, and examples include synthetic and natural polymeric compounds such as polyvinyl alcohol, casein, starch and its derivative, Arabic rubber, methyl cellulose, carboxymethylcellulose, polyacrylic acid, latex such as styrene-butadiene copolymer latex, acrylic acid ester latex.

[0047] The amount of binder, though not limited, is generally 5-40% by weight, preferably 10-30% by weight based on the weight of total solid part of the color developer coating liquid.

[0048] For the present invention, inorganic pigments may be used such as zinc oxide, zinc carbonate, calcium carbonate, magnesium carbonate, barium carbonate, magnesium sulfate, barium sulfate, titanium oxide, talc, kaolin, active china clay, diatomite, zinc hydroxide, aluminum hydroxide, magnesium hydroxide, alumina and silica; and organic paints such as styrene microball, nylon particle, urea formaldehyde filler, polyethylene particles, cellulose filler and starch particles.

[0049] There is no special limit on the amount of pigments, but should be 30-90% by weight based on the weight of the total solid part of the color developer coating liquid.

[0050] In addition, various additives (e.g., UV absorbing agent, defoaming agent, pH adjusting agent, viscosity control agent, plasticizer and organic polymeric compound) may be added to the coating liquid, if necessary.

[0051] Color development sheet may be prepared by applying on a support (e.g., plastic sheet, synthetic paper, or a combination thereof) the coating liquid prepared as above using known means, for example, air knife coater, blade coater, roll coater, seize press coater, curtain coater or shortduwell coater to form a color development layer.

[0052] No special limit exists on the weight (coating, amount) of the color developer layer on the support, but the dry weight may be at least 0.5g/m², preferably, 0.5 to 10g/m². Furthermore, the content of polyvalent metal salts of salicylic acid resin of the present invention in the color developer layer is generally 5% by weight or more, preferably 5-70%.

[0053] In the preparation of color development sheet of the present invention, other color developers may be used with the polyvalent metal salts of salicylic acid to the extent that the effect of the present invention is not impaired. Examples of such other additives include acidic clay mineral such as acidic China clay, active China clay, attapulgit and bentonite; phenol resin such as phenol-formaldehyde resin, phenol-salicylic acid formaldehyde resin; zinc salt of aromatic carboxylic acid such as phthalic acid, salicylic acid, 5-cyclohexylsalicylic acid, 5-t-octylsalicylic acid, 5-nonylsalicylic acid, 3,5-dinonylsalicylic acid, 3-(α -methylbenzyl)salicylic acid, 5-(α -dimethylbenzyl)salicylic acid, 5-phenylsalicylic acid, 3,5-di(α -methylbenzyl)salicylic acid, 3,5-di(α , α -dimethylbenzyl)salicylic acid and 3,5-di-t-butylsalicylic acid.

[0054] The color development sheet according to the present invention is not limited in shape, but the following may be enumerated:

- 1) CF sheet that may be used in combination with CB sheet whose back side is coated with micro-capsule containing electron donating color-developing compound and capsule oil
- 2) CF/CB sheet wherein micro-capsule layer is established in back side of sheet, and developer layer is established on the surface of the sheet inserted between CB sheet and CF sheet in order for multiple copy
- 3) Monocopy sheet wherein micro-capsule and developer are coated in one side of the sheet

[0055] The present invention is further illustrated by the following Examples below, which should not be construed as limiting the scope of the invention.

55 Example 1

[0056] 204g of salicylic acid, 20g of zinc acetate (dihydrate), 20g of zinc stearate and 100g of styrene were charged into a glass reaction vessel. The mixture was stirred at elevated temperature of 140°C. 287g of Styrene was dropped

to the mixture over 3 hours and stirred at the same temperature for two hours. Temperature of the reaction mixture was lowered to 115°C and 60g of zinc oxide was added. After two hours of reaction at the same temperature, 655g of zinc salt of salicylic acid resin was obtained (yield: 94.8%, softening point: 98°C, average molecular weight: 670).

[0057] To the resin thus obtained, 30g of polyvinyl alcohol, 3g of sodium dodecylbenzene sulfonate and 840g of purified water were added, and then obtained 1528g of aqueous dispersion of which the solid content is 45% and the average particle size is 0.38µm.

Example 2

[0058] 68g of salicylic acid, 0.8g of zinc oxide and 128g of styrene were charged into a glass reaction vessel. The resulting mixture was stirred at elevated temperature of 155°C, and reacted for 2-3 hours. At 150°C, 19.3g of zinc oxide was added. The reaction was conducted for 2 hours at 140-155°C to obtain 240g of zinc salt of salicylic acid resin (yield: 94.4%, softening point: 98°C, average molecular weight: 690)

[0059] The resin thus obtained was emulsified with 10g of polyvinyl alcohol and 262g of purified water to obtain 476g of aqueous dispersion of which the solid content is 45% and the average particle size is 0.41 µm.

Example 3

[0060] Except for using styrene in an amount of 400g instead of 387g, and using 30g of zinc stearate with no use of zinc acetate, the reaction was conducted in the same manner as in Example 1, and 640g of zinc salt of salicylic acid resin was obtained (yield: 92.2%, softening point: 99°C, average molecular weight: 715).

Example 4

[0061] Except that styrene was used in an amount of 120g instead of 100g, that dropping amount was reduced from 287g to 267g, and that 30g of zinc acetate was used with no use of zinc stearate, reaction was conducted in the same manner as in Example 1 to obtain 656g of zinc salt of salicylic acid resin (yield: 96.3%, softening point: 110°C, average molecular weight: 730).

Example 5

[0062] According to the method as in Example 1 except that 15g of zinc caprylate was used instead of zinc acetate and zinc stearate, 632g of zinc salt of salicylic acid resin was obtained (yield: 94.9%, softening point: 96°C, average molecular weight: 680).

Example 6

[0063] In the same manner as in Example 1 except that 184g of salicylic acid and 22.5g of 4-methylsalicylic acid were used instead of 204g of salicylic acid, the reaction is conducted to prepare 657g of zinc salt of salicylic acid (yield: 94.7%, softening point: 112°C, average molecular weight: 705).

Example 7

[0064] In the same manner as in Example 1 except for using 256g of styrene and 35g of 4-methylstyrene instead of 287g of styrene, 658g of zinc salt of salicylic acid resin was obtained (yield: 94.7%, softening point: 113°C, average molecular weight: 710)

Example 8

[0065] 204g of salicylic acid, 30g of zinc acetate and 387g of styrene were charged into a glass reaction vessel. After stirring for 3 hours at 150°C, 60g of zinc oxide was added at 135°C, and reacted for 2 hours to obtain 635g of zinc salt of salicylic acid resin (yield: 93.2%, softening point: 99°C, average molecular weight: 685).

Example 9

[0066] In glass reaction vessel, 129g of styrene, 36g of zinc oxide and 80g of salicylic acid were charged, and the mixture was stirred for 5 hours at elevated temperature of 157°C, and 245g of zinc salt of salicylic acid resin was obtained (yield: 85%, softening point: 114°C, average molecular weight: 803).

Example 10: Preparation of a color development sheet for pressure-sensitive copy

[0067] According to the following process using the aqueous dispersion obtained from example 1 as a color developer, a color development sheet for pressure-sensitive copy was prepared.

5 [0068] Dispersion (A) was obtained by dispersing a mixture with the following composition. Herein, the pH was adjusted to 7.5.

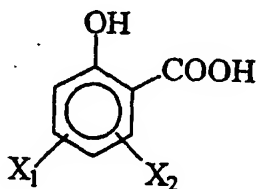
Water	105.8g
Calcium carbonate	24 g
10 Clay	49g
Oxidized starch (20%)	22.2g
Latex (48%)	11.6g
Dispersant (40%)	6.8g
Lubricant (50%)	4.5g
15 Ammonia water	adequate amount

[0069] 2.61g of the color developer obtained by Example 1 was mixed with 22.4g of dispersion (A), and the resulting liquid was coated in a dried amount of 5.0g/m² onto a paper (50g/m²) to obtain a color development sheet.

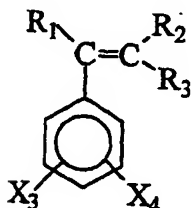
20 Claims

1. A process for preparing polyvalent metal salts of salicylic acid resin comprising:

25 reacting salicylic acid of formula 1 or its derivative and styrene of formula 2 or its derivative in the presence of a zinc salt of an organic carboxylic acid and/or a polyvalent metal compound at 50-200°C, and reacting the resulting reaction product with a polyvalent metal compound.



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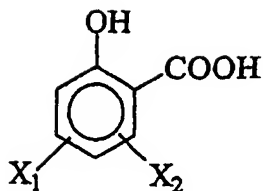


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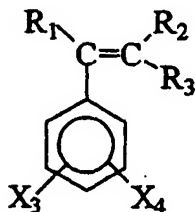
50 wherein, each X₁ and X₂ is hydrogen, alkyl, alkoxy or halogen, and each of R₁, R₂ and R₃ is hydrogen or alkyl, and each of X₃ and X₄ is hydrogen, alkyl, alkoxy, aralkyl, aryl or halogen.

2. A process for preparing polyvalent metal salts of salicylic acid resin, comprising:

55 reacting salicylic acid of formula 1 or its derivative and styrene of formula 2 or its derivative in the presence of a polyvalent metal compound or a mixture of a polyvalent metal compound and a zinc salt of an organic carboxylic acid at 50-200 °C.



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2

wherein, each X_1 and X_2 is hydrogen, alkyl, alkoxy or halogen, and each of R_1 , R_2 and R_3 is hydrogen or alkyl, and each of X_3 and X_4 is hydrogen, alkyl, alkoxy, aralkyl, aryl or halogen.

3. The process according to Claim 1 or 2, wherein the zinc salt of organic carboxylic acid is at least one selected from zinc benzoate, zinc caprylate, zinc stearate and zinc acetate.
4. The process according to Claim 1 or 2, wherein the polyvalent metal compound is at least one selected from zinc sulfate, magnesium sulfate, calcium sulfate, aluminum sulfate, zinc chloride, magnesium chloride, calcium chloride, barium chloride, nickel chloride, cobalt chloride, aluminum chloride, zinc acetate, manganese acetate, zinc nitrate, zinc oxide and zinc hydroxide.
5. Polyvalent metal salts of salicylic acid resin obtainable by the process of Claim 1 or 2.
6. An aqueous dispersion comprising the polyvalent metal salts of salicylic acid resin of Claim 5 dispersed in water.
7. A color development sheet prepared from the polyvalent metal salts of salicylic acid resin of Claim 5.

